- Technical Paper -

# INFLUENCES OF NANO-TIO<sub>2</sub> PARTICLES ON ALTERATION OF MICROSTRUCTURE OF HARDENED CEMENT

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#### ABSTRACT

This paper reports the influence of nano-TiO<sub>2</sub> given to alteration of the microstructure of hardened cement pastes with drying process. Cement pastes containing 3% nano-TiO<sub>2</sub> (in addition outside split) by mass of cement were prepared. In hydration process, nano-TiO<sub>2</sub> was delayed a long-term hydration of belite (C<sub>2</sub>S), and suppressed the production of Ca(OH)<sub>2</sub>. In drying process, the TiO<sub>2</sub> added paste shrunk larger than non-added paste. It was suggested that this phenomenon may be due to a decrease in Ca(OH)<sub>2</sub> production by the addition of nano-TiO<sub>2</sub>.

Keywords:  $TiO_2$  nanoparticle, calcium silicate hydroxide, calcium hydroxide, hydration, drying shrinkage strain, X ray diffraction

# 1. INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) is relatively cheap and chemically stable, and widely used as a photocatalyst. Also, nanoparticles having a diameter of  $1 \sim 100$ nm is simply not only small in size, physical and chemical properties are significantly different than the particle size with several hundred nanometer or more [1]. With the development of nanotechnology in construction and building materials, TiO<sub>2</sub> nanoparticles have been used as admixture for concrete in last decades.

Recently, some investigation revealed that the influences of nano-TiO<sub>2</sub> are not only the depollution self-cleaning performance, but also the and improvement of the inherent properties of the hardened cement pastes [2-6]. Chen et al. [2] investigated the effects of blending nano-TiO<sub>2</sub> into cement pastes and mortars on the hydration and properties of the hydrated cement pastes. Through their experimental studies, the addition of nano-TiO2 powders significantly accelerated the hydration rate and promoted the hydration degree of the cementitious materials at early ages. Further, during the hydration process, nano-TiO<sub>2</sub> was inert and stable, so  $TiO_2$  was confirmed to be a non-reactive fine filler that acted as potential nucleation sites for the accumulation of hydration products. Also, the total porosity of TiO<sub>2</sub> blended pastes was decreased and pore volume mainly decreased within the capillary pore range. It is suggested that the addition of TiO<sub>2</sub> affects the change in microstructure. Feng et al. [3] revealed that, by the admixing of nano-TiO<sub>2</sub> into cement, modification of microstructures in nano-scale increased the amount of cementitious phase in the paste, decreased the micro-porosity and amount of internal micro-cracks and defects. formed a denser microstructure, and led the formation to of needle-shaped nanoprecipitates.

In addition, the admixing of nano-TiO<sub>2</sub> into cement enhances the compressive strength and the flexural strength [2-5]. This is due to more formation of hydration products and denser microstructure in presence of nano-TiO<sub>2</sub>

On the contrary, research on the influence of the shrinkage behavior of cement paste or concrete by the addition of nano-TiO<sub>2</sub> is scare. Hasebe and Edahiro [7] measured drying shrinkage strain of concrete which was mixed nano-TiO<sub>2</sub> at various substitutions proportions, the specimens mixed with nano-TiO<sub>2</sub> tend to shrink overall larger than that of non-miscible. Experimental study on the addition of nano-TiO<sub>2</sub> on hardened alkali-activated slag paste shows reduction of the shrinkage behavior, for example [8], is conducted in the range of up to age of 28 days and includes the effects of the autogenous shrinkage.

Based on our literature survey, previous studies have focused on the effect of the hydration process and we concluded that little research on the impact of microstructure in mature paste especially for the first drying process has been conducted and such research is needed for application.

The aim of this paper is to elucidate the influence of nano-TiO<sub>2</sub> on the microstructure of hardened cement pastes under the first drying process. Reference samples (plain) and cement/TiO<sub>2</sub> composite samples containing 3% nano-TiO<sub>2</sub> (by extra-addition) by mass of cement were prepared. After the almost fully hydration obtained after curing condition with wet condition for 6 months, length change isotherms for samples dried under different relative humidity, sorption isotherms, X-ray diffraction measurements (XRD) and Rietveld analysis were conducted.

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#### EXPERIMENTAL PROCEDURE 2.

#### 2.1 Materials and sample preparation

(1)  $TiO_2$  nanoparticles

We used nano-TiO<sub>2</sub> provided by the Tayca Corporation. The TiO<sub>2</sub> suspension was dried for one week, the preparation of the test specimen was used as a powder state nano-TiO2. The SEM image of nano-TiO<sub>2</sub> powder is shown in Fig. 1.

(2) Cement paste

White Portland cement is used for the binder of cement paste. The chemical components, physical properties, and mineral compositions of White Portland cement are shown in Table 1 and 2. The mineral composition was determined by XRD measurements and Rietveld analysis.

The water-cement ratio of cement pastes were 0.40 and 0.55. Reference samples which do not contain the TiO<sub>2</sub> nanoparticles named as W40-Plain and W55-Plain. On the other hands, specimens of W/C with 0.40 and 0.55 containing TiO<sub>2</sub> powder were named as W40-TiO<sub>2</sub> and W55-TiO<sub>2</sub> respectively. The amount of nano-TiO<sub>2</sub> powder externally added to the cement was 3% by mass cement of each water-cement ratio condition. Cement paste (ca. 300g) was mixed in a 500 cc vacuum mixer for 3 min after the water was added. For dispersion of TiO<sub>2</sub> particles in the cement paste and avoiding the agglomeration, sonication process was applied in case of W55-TiO<sub>2</sub> and W40-TiO<sub>2</sub> for 1.5 min. Then, paste was scraped and mixed for a further 3 min by the mixer. All the materials were stored in a thermostatic chamber at  $20 \pm 1^{\circ}$ C for 1 day prior to mixing. The mixing was performed at room temperature (ca. 20 °C) and the specimens were then immediately moved to a thermostatic chamber again. To minimize segregation, the paste was remixed every 30 min, for 6 hours. The specimens were placed into vial containers with  $\phi 15$  mm and 80mm depth and they were stored in a thermostatic chamber at a temperature of  $20 \pm 1^{\circ}$ C. They were demolded after 4 days, and samples were immersed in lime-saturated water for 6 months.

#### 2.2 Experimental selection

#### (1) XRD/Rietveld analysis

The hardened cement paste (hcp) specimens were analyzed by powder X-ray diffraction (D8 advance, Bruker AXS) after curing for 6 months. All the hcp specimens were submerged in acetone for 6



Fig. 1 nano-TiO<sub>2</sub> SEM image

hours and dried under vacuum for several minutes with an aspirator. The specimens were stored at 11% RH (equilibrium to CaCl<sub>2</sub> solution) and 20 °C for 2 weeks. The specimens were ground in a ball mill, and corundum powder (10 mass %) was added to the sample powder as a standard reference. The XRD conditions were as follows: tube voltage, 50 kV; tube current, 250 mA; scan range of 20, 5-65°; step width, 0.02°; scan speed, 2°/min. The software used for the Rietveld analysis was TOPAS Ver. 4.0 (Bruker AXS). In the Rietveld analysis, the quantified phases were gypsum, basanite, portlandite, ettringite (AFt), monosulfate (AFm), calcite, as well as typical cement materials, such as alite  $(C_3S)_{\pi}$  belite  $(C_2S)$ , cubic- $C_3A$ , and C<sub>4</sub>AF. The details was shown in the our previous study [9]

The samples were measured 3 times for each parameter. After the Rietveld analysis, the degrees of hydration of the clinker minerals were calculated. (2) Short-term length change isotherm (SLCI)

For measuring SLCI, samples  $3 \times 3 \times 1$  mm in size were cut from the saturated hcp specimens for use with a more rapid experimental technique in which these very small specimens were subjected to forced drying under an RH-controlled air flow. This experiment carried out on W55-Plain and W55-TiO<sub>2</sub>. Length change isotherms for samples dried under different RHs at 20 °C were obtained with a thermomechanical analyzer (TMA) coupled with an RH generator (TMA4000SA and HC9700, Bruker AXS). Length changes were measured with a linear variable differential transfer (LVDT) with a precision of 0.5 µm,

	Table 1 Chemical composition of white cement								
Ig.loss	$SiO_2$	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	$SO_3$	Na <sub>2</sub> O	K <sub>2</sub> O	Cl
(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
3.18	22.68	4.50	0.19	65.07	1.19	2.75	0.06	0.07	0.004

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Table	Table 2 Mineral composition of white cement determined by XRD and Rietveld analysis						
$C_3S$	$C_2S$	C <sub>3</sub> A	Periclase	Bassanite	Gypsum	Calcite	
(%)	(%)	(%)	(%)	(%)	(%)	(%)	
51.6	35.1	5.88	6.08	2.75	2.75	3.76	

C:CaO, S:SiO<sub>2</sub>, A:Al<sub>2</sub>O<sub>3</sub>, M:MgO

a minimum resolution of 0.0025  $\mu$ m, and a contact load of 0.098 N. The samples were incrementally dried from saturated state to 10% RH, after which they were incrementally re-humidified back up to 90% RH. All the processes were conducted at 20 ± 0.1°C. For each step the RH of the flowing atmosphere was kept constant for at 5 hours.

(3) Short-term sorption isotherm

In this experiment, the specimens of W55-Plain and W55-TiO2 were measured. The data are controlled by using thermogravimetry analyzer coupled with the RH generator (TG-DTA 2000SA and HC9700, Bruker AXS). For measuring short-term sorption isotherms, powdery samples were prepared by grinding the saturated hcp specimens. Just before the experiment, the samples were re-saturated with water for several min and then placed in the equipment. The experiment was started after samples achieved water saturated condition. The target RH values for the samples were 90, 80, 60, 40, 20, 10%, after 10% RH, the samples were incrementally re-humidified back up to 90% RH. All the processes were conducted at  $20 \pm 0.1$  °C. For each step the RH of the flowing atmosphere was kept constant for at 5 hours. In parallel with this experiment, representative powder samples (ca 20 mg) from the powdered cement pastes were heated at 105°C under nitrogen gas flow to obtain the saturated water content. process conducted This was by thermogravimetry/differential thermal analyzer (TG-DTA, Bruker AXS, TG-DTA 2010 SA).

#### 3. RESULTS AND DISCUSSIONS

Figure 2 presents the degrees of hydration of the minerals in hcp after lime-saturated water curing of 6 months. The degree of hydration of aluminate phases was 100% of all specimens with every parameter. For the hydration rate of alite, the paste containing nano-TiO<sub>2</sub> powder showed slightly smaller value. On the contrary, the degree of hydration of belite was largely reduced by the addition of nano-TiO<sub>2</sub> regardless of the water-cement ratio. Chen et al. [2] reported that the addition of TiO<sub>2</sub> nanoparticles accelerate the hydration degree of the cementitious materials at early hydration stages. However, from this experimental data, in terms of long-term hydration, the addition of nano-TiO<sub>2</sub> was suggested to stagnate the hydration, especially in the case of belite.

Figure 3 shows the amount of calcium hydroxide  $(Ca(OH)_2)$  and calcium silicate hydrate (C-S-H) in hcp after 6 months curing, calculated from the Rietveld analysis. Consistently for each water-cement ratio, hydration amount of  $Ca(OH)_2$  and C-S-H tended to decrease by the addition of nano-TiO<sub>2</sub> particle.

In previous studies, Chen et al. [2] have pointed out that  $TiO_2$  is inert and stable during the cement hydration process, and has no pozzolanic reactivity. Additionally, the direct reaction of Ca(OH)<sub>2</sub> and TiO<sub>2</sub> to form CaTiO<sub>3</sub> generally occurs only at temperature over 1000 K [3]. He and Shi observed the nanoparticles modified mortar specimens with a field emission scanning electron microscope (FESEM), and reported



Fig. 2 Degrees of hydration of the alite, belite, and aluminate phases. Samples were cured at 6 months underwater.



Fig. 3 The mass ratio of Ca(OH)<sub>2</sub> and C-S-H of White Portland cement paste determined by powder XRD and Rietveld analysis.
The sample was cured at 11% RH. The amount of externally-added nano-TiO<sub>2</sub> powder is included in the mass of anhydrous hcp.

that Ca(OH)<sub>2</sub> plate crystals were much less identifiable than no-admixed sample [10]. It has been suggested that the addition of TiO<sub>2</sub> affects reducing the size of its plate crystals. Further, they summarized the mechanisms responsible for the effect of nanoparticles on the impermeability of mortars as follow: (1) working as nanosized fillers and lead to a denser and less permeable microstructure, (2) acting as a nucleus to guide the formation and growth of cement hydration products, (3) promoting the formation of high density C-S-H structures via parallel packing. Acting as a nucleus affects also inhibiting the growth of Ca(OH)<sub>2</sub> crystals [10].

In contradiction to the existing research about hydration process and formation of microstructure, present experimental results exhibited that nano-TiO<sub>2</sub> particle stagnated the reaction of belite, and also depressed the precipitation of Ca(OH)<sub>2</sub> in cement paste. This might be through the solution-precipitation mechanism in pore solution and Ca(OH)<sub>2</sub> [11,12,13], but further investigation is needed for clarification.

Figure 4 shows length change isotherms obtained from SLCI experiments. Also, water sorption

isotherms obtained from short-term sorption isotherm experiments are presented in Fig. 5.

In Fig. 4, drying shrinkage strain of W55-TiO<sub>2</sub> was larger than that of W55-Plain. Process from the saturated state (100% RH) to 10% RH in Fig. 4 represents the first desorption process of hcp. The shrinkage of hcp during the first desorption process is normally accompanied by microstructural changes [14]. But the shrinkage strain of SLCI is less affected by the microstructural changes caused by a short drying time, while some impact of C-S-H colloidal alteration under the first desorption process is inevitable [15]. The difference of the shrinkage strain between W55-Plain and W55-TiO<sub>2</sub> is considered to be divided into 2 stages in Fig. 4. First stage, from saturated state to 40% RH, the difference of them became larger as the gradually dried. Second, from 40% to 10% RH, and re-humidified process, the difference was approximately equivalent to the value of 40% RH for desorption process. Therefore, the impact on the drying shrinkage of TiO<sub>2</sub> addition is shown in the range from 100% RH to 40% RH.

In Fig. 5, saturated water content of W55-Plain and W55-TiO<sub>2</sub> were almost the same, but water content of W55-Plain was always smaller than that of W55-TiO<sub>2</sub> through the desorption process and the re-adsorption process. The difference of water content between W55-Plain and W55-TiO<sub>2</sub> became larger from 100% to 40% RH. In the process below 40% RH, this difference was generally the same except for the values of 90% RH in the re-humidified process.

Figure 6 shows the shrinkage strain – water content relationship of W55-Plain and W55-TiO<sub>2</sub>, and is what integrates of the results of Fig. 4 and Fig. 5. In Fig. 6, W55-TiO<sub>2</sub> was a tendency shrinkage strain increases, even large water content as compared to W55-Plain.

From a view of hypothesis that system containing nano-TiO2 particles tend not to precipitated the  $Ca(OH)_2$  and this mechanism is active even in the first desorption process, increase in the drying shrinkage from 100% RH to 40% RH can be explained. Because the precipitation of  $Ca(OH)_2$  is simultaneously accompanied under the evaporation of pore solution under the first desorption, and this precipitated  $Ca(OH)_2$  should restrain the C-S-H colloidal shrinkage behavior [16].

It should be noted that the range from 100% RH to 40% RH is corresponding to the region in which colloidal feature of C-S-H is observed [14] and the irreversible shrinkage is produced here [15]. Therefore, the balance of C-S-H and pollandite might be key parameter for the shrinkage behavior in this range.

Table 3 summrise the mass ratio of Ca(OH)<sub>2</sub> to C-S-H represented in Fig. 3, the ratio of Ca(OH)<sub>2</sub> and C-S-H (Ca(OH)<sub>2</sub> / C-S-H ratio) and the shrinkage strain of W55-Plain and W55-TiO<sub>2</sub> from 100% to 40% RH in the first drying process shown in Fig. 4. In Table 3, it is cleared that W55-Plain contains more C-S-H and Ca(OH)<sub>2</sub>, and is larger Ca(OH)<sub>2</sub> / C-S-H ratio, in comparison with W55-TiO<sub>2</sub>. This mechanism is very active in the 100% RH to 40% RH and the first



Fig. 4 Length-change isotherms of W55-Plain and W55-TiO<sub>2</sub>



Fig. 5 Sorption isotherms of W55-Plain and W55-TiO $_2$ 

The amount of externally-added nano- $TiO_2$  powder is included in the mass of dried hcp.



Fig. 6 Shrinkage strain – water content

desorption process. Therefore, the precipitated  $Ca(OH)_2$ under this region is deduced to have an impact to restrain the agglomeration of C-S-H as colloidal materials. From this aspect, the size of portlandite might be important as well. It has been reported that the size of portlandite crystals become smaller by the addition of TiO<sub>2</sub> nanoparticles [10], therefore, the change in size of portlandite is another possible mechanism to mitigate the colloidal agglomeration of C-S-H.

To clarify the impact of  $TiO_2$  on the shrinkage

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Parameter	C-S-H	Ca(OH) <sub>2</sub>	Ca(OH) <sub>2</sub> / C-S-H ratio	Shrinkage strain (from 100% to 40% RH)	
	(g/g-dried hcp)	(g/g-dried hcp)	(-)	(μ)	
W55-Plain	$0.654 \pm 0.022$	$0.169 \pm 0.009$	0.259	4678	
W55-TiO <sub>2</sub>	$0.633 \pm 0.014$	$0.142 \pm 0.003$	0.224	5616	
W40-Plain	$0.601 \pm 0.037$	$0.154 \pm 0.008$	0.257	-	
W40-TiO <sub>2</sub>	$0.588\pm0.039$	$0.140\pm0.006$	0.237	-	

Table 3 Ca(OH)<sub>2</sub> / C-S-H ratio and shrinkage strain of from saturated state to 40% RH in the first drying process

behavior, FE-SEM observation, additional short-term length change isotherm of W40-TiO<sub>2</sub> and W40-Plain, and impact of density of nano-TiO<sub>2</sub> particles on the mechanical properties are needed.

## 4. CONCLUSIONS

The influence of the addition of nano- $TiO_2$  particles on shrinkage behavior of hardened cement paste is investigated through comparison of the reference white cement paste with that containing additional 3 mass% to cement of nano- $TiO_2$  particles.

The followings are newly obtained by the experiment:

- (1) In matured state (ca 6 month under the room temperature curing with lime-saturated water), the addition of nano-TiO<sub>2</sub> retarded the belite ( $C_2S$ ) reaction.
- (2) In the hydration process, the addition of nano- $TiO_2$  depress the precipitation of portlandite.
- (3) Short-term sorption isotherms showed water content of cement paste containing nano-TiO<sub>2</sub> particles is larger than that of reference paste through the first drying process and the re-adsorption process.
- (4) Short-term length change isotherms showed that the drying shrinkage strain of nano-TiO<sub>2</sub> added cement paste is larger than that of reference paste. Especially, from 100% to 40% RH in the first drying process, the shrinkage of cement paste containing nano-TiO<sub>2</sub> particles is increased significantly. This phenomenon can be explained by the reduction of precipitation of portlandite, which has a role to restrain the colloidal agglomeration of C-S-H under the first desorption process.

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